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1. REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
2. REPORT NUMBER <b>AFOSR-TR-81-0325</b>		3. GOVT ACCESSION NO. <b>AD-A097410</b>	
4. TITLE (and Subtitle) <b>*Model Systems for the Epitaxial Growth and Capping of GaAs*</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Final report Feb 80 - July 80</b>	
6. AUTHOR(s) <b>Richard G. Yalman</b>		7. CONTRACT OR GRANT NUMBER(s) <b>AFOSR-80-0121</b>	
8. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Antioch College Yellow Springs, Ohio 45387</b>		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>61102F 162306/D9</b>	
10. CONTROLLING OFFICE NAME AND ADDRESS <b>Air Force Office of Scientific Research Bolling Air Force Base, Washington, D.C. 20332</b>		11. REPORT DATE <b>11/1980</b>	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES <b>34</b>	
14. DISTRIBUTION STATEMENT (of this Report) <b>Approved for public release, distribution unlimited.</b>		15. SECURITY CLASS. (of this report) <b>Unclassified</b>	
16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		17. SUPPLEMENTARY NOTES <b>To be presented at the "Fifth International Conference on Vapor Growth and Epitaxy", San Diego, July 19-24, 1981.</b>	
18. KEY WORDS (Continue on reverse side if necessary and identify by block number) <b>Epitaxy, Epitaxial Growth, Dopants, Gallium Arsenide</b>		19. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>A computer program has been written for the CVD of epitaxial GaAs and InP in a three bubbler, two boat silica glass reactor using the Ga/AsCl<sub>3</sub>/H<sub>2</sub> and In/PCl<sub>3</sub>/H<sub>2</sub> techniques, respectively. The data bank contains the most recent enthalpy and free energy values. The latter are in the form of polynomials and, where necessary, recalculated from heat capacity or spectroscopic data. The importance of correct enthalpy values for computing As<sub>2</sub>/As ratios and the concentrations of volatile silicon compounds is discussed in detail. Calcula-</b>	

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20. ABSTRACT (cont.)

tions were made by iterative approximations rather than using the minimized total Gibb's free energy method. The difference in these methods is examined.

The chemistry of the transport system has been examined in stages in the high temperature source region. Three models are proposed for the flat profile reaction of  $\text{HCl}$  with the arsenic saturated source material which is covered by a crust of GaAs (or InP). In Model I  $\text{HCl}$  reacts only with GaAs. In Model II a series of reactions occur resulting in constant crust throughout the growth period. In Model III there is a constant build-up of crust during the growth period. Additional reactions occur when there is a temperature gradient in the source. Actual experimental data for Ga/As ratios corresponds to a combination of these models.

The effect of  $\text{AsCl}_3$  input,  $\text{H}_2$ -inert gas carrier mixtures and the addition of  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{NH}_3$  were studied. The program includes subroutines for intentional dopants. For example, the observed dependency of S-doping on  $\text{AsCl}_3$  input can be explained by the formation of  $\text{Ga}_2\text{S}_3$ . The program also supplies information regarding supersaturation, i.e. nucleation, as well as relative rates of growth and etching of the epi layer.

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# AFOSR-TR- 81 - 0325

MODEL SYSTEMS FOR THE EPITAXIAL GROWTH AND CAPPING OF GaAs

Richard G. Yalman  
1980

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## INTRODUCTION

Epitaxial GaAs is used in a variety of electronic devices (LEDs, FETs, IMPATTs, etc.). The relatively wide band gap and high electron mobility of GaAs gives it an edge over silicon in microwave applications including solid state transmitters and receivers for radar and communication systems. This requires materials with less than  $10^{14} \text{ cm}^{-3}$  impurities and mobilities greater than 120,000 at 77 K. High purity epitaxial GaAs has been prepared using the single bubbler, single boat Ga/AsCl<sub>3</sub>/H<sub>2</sub> technique.<sup>1,2</sup> Good results have also been obtained by modifications of the basic technique using solid GaAs<sup>3</sup>, a two bubbler system<sup>4</sup>, flat furnace profiles<sup>5,6</sup>, H<sub>2</sub>-inert gas mixtures<sup>7,8</sup> and inert gases<sup>9</sup>. In each of these modifications gallium is transported as GaCl<sup>10</sup> together with a mixture of As<sub>2</sub> and As<sub>4</sub> from a high temperature source region via a carrier gas to a low temperature deposition region where epitaxial GaAs is grown on a high resistance GaAs substrate.

Unfortunately the preparation of epitaxial GaAs is still largely an art and consistently good material cannot be obtained. This results in low yields, high cost and components of questionable reliability. To overcome these problems the Electronic Research Branch of the Avionics Laboratory, WPAFB has initiated a program to re-examine the source and substrate materials and the transport and growth conditions required for the preparation of high mobility GaAs using a new reactor system containing two boats and three bubblers (Fig. 1). In this system purified hydrogen is used as a carrier gas and supplied to a manifold consisting of three mass controllers and three arsenic trichloride bubblers maintained at constant temperature. The arsenic trichloride from the first bubbler reacts with hydrogen gas in the high temperature region of the reactor tube to form hydrogen chloride and an equilibrium mixture of HCl and As<sub>2</sub> and As<sub>4</sub> (equation 1).



The hydrogen chloride formed in reaction (1) reacts with the walls of the silica glass reactor to form chlorosilanes and with the Ga and/or GaAs in the boat to form GaCl. Elemental arsenic also reacts with Ga in the boat to form a saturated phase  $Ga_{1-x}As_x$ <sup>11</sup> and GaAs. Arsenic trichloride from the second bubbler passes through a cracking furnace where reaction (1) again occurs. The elemental arsenic is condensed and the purified HCl is allowed to pass over gallium in the second boat where reaction (2) occurs.



Finally arsenic trichloride from the third bubbler enters the high temperature region of the reactor tube beyond the boat region. In the low temperature region epitaxial layers of GaAs are formed on Cr-, O- or Sn-doped substrates according to the overall reaction



where  $As_n$  is the equilibrium mixture of  $As_2$  and  $As_4$ .

By using the two boat, three bubbler system a number of parameters can be investigated: flow rates, Ga/As and Ga/Cl ratios,  $H_2$ /inert gas ratios, the reactor temperature profile and the source and deposition temperatures. In particular the effect of these parameters on the stoichiometry of the epilayers will be investigated, i.e. what parameters control the formation of n and p type materials.

#### OBJECTIVES

In order to gain a better understanding of the chemistry of the system and to contribute to the experimental design of the proposed investigations, it seemed worthwhile to develop a computer program which would incorporate all of the features of the reactor, including all of the outlined parameters and possible chemical reactions. The purpose of this report is to discuss the chemistry of the Ga/AsCl<sub>3</sub>/H<sub>2</sub> and related systems, to briefly outline the salient features of the computer program and its thermodynamic data bank and to report on some of the findings

resulting from the chemical analysis and computer calculations.

## FINDINGS

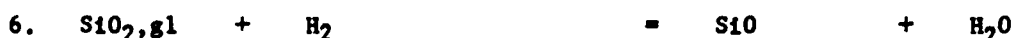
### The Chemistry of the Ga-AsCl<sub>3</sub> System

In the high temperature (850°C) region of the reactor and in the cracking furnace arsenic trichloride and hydrogen react to form HCl and elemental arsenic

(1). In addition the equilibrium



is established. Next the hot HCl reacts with the hot silica glass of the inlet tube and reactor walls to form a series of chlorosilanes (5-8) SiO, SiCl<sub>2</sub> and elemental silicon vapor, Si<sub>g</sub>.



Numerous reactions occur with the source materials. The boat itself reacts with gallium (reaction 9) to form volatile SiO and Ga<sub>2</sub>O<sup>12</sup>. The chlorosilanes also



react with gallium forming additional silicon vapor which can dissolve in the

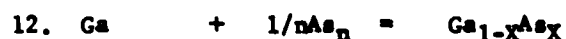


gallium<sup>13</sup>. Elemental silicon can also react with hydrogen and the HCl introduced via AsCl<sub>3</sub> beyond the boat region to reform chlorosilanes.

Chlorosilanes have been used<sup>14</sup> as sources of silicon in the preparation of Si-doped epitaxial GaAs. It is clear therefore that there are ample sources of unintentional Si-doping in the Ga/AsCl<sub>3</sub>/H<sub>2</sub> system. But it has also been found that Si-doping decreases with increasing AsCl<sub>3</sub> input<sup>15</sup>.

Arsenic formed either by reaction (1) in an hydrogen atmosphere or by

reaction (11) in an inert atmosphere dissolves in gallium forming  $Ga_{1-X}As_X$ <sup>11</sup>



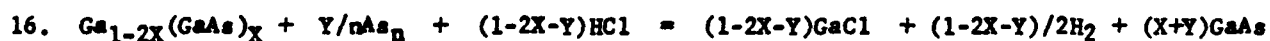
where X is the atomic fraction of arsenic in the liquids phase in equilibrium with gallium arsenide. Unfortunately this system readily supersaturates, and upon nucleation forms a crust of GaAs<sup>16</sup>. It is not known as to whether this crust is completely uniform and/or porous during the growth period.

If the assumption that the crust is uniform and nonporous and the temperature profile over the source material is flat, then the only material exposed to the gas phase is GaAs which reacts with HCl (13).



Reaction (13) is the reverse of reaction (3).

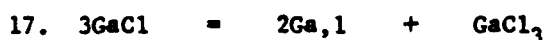
If the crust of GaAs is porous, broken or there is a temperature gradient along the source material, additional reactions must be considered.



Reaction (14) corresponds to a steady state condition with respect to the crust, i.e.  $d(GaAs)/dt = 0$ , and slightly increases the amount of arsenic in the gas state. Reaction (15) corresponds to the build up of crust material from dissolved arsenic. Reaction (16) is a general reaction for the simultaneous formation of GaAs from dissolved arsenic and from arsenic dissolving in the high temperature region of the boat and precipitating as GaAs in the low temperature region of the boat. This formation corresponds to Shaw's<sup>16</sup> description of crusting under a temperature gradient. Finally reactions (14) and (15) could occur if gallium diffuses through GaAs.

Volatile GaCl produced either by the reaction of arsenic trichloride with

gallium or by the reactions of hydrogen chloride with the Ga-As system passes downstream via the carrier gas to the cooler deposition region. Here the overall reaction for the growth of GaAs is given by equation (3). Although the mechanism of this reaction is not known, it has been suggested that hydrogen <sup>17</sup> is involved in the desorption of chloride from absorbed GaCl on the surface of the growing GaAs in the Ga/AsCl<sub>3</sub>/H<sub>2</sub> system whereas the removal of chloride in the inert gas systems <sup>3</sup> is due to the disproportionation reaction.



Equally unclear is the role of either As<sub>2</sub> or As<sub>4</sub> on the growth of the epi layer.

Additional reactions included in this study are those related to the intentional doping of GaAs by sulfur using H<sub>2</sub>S as the source of the dopant.



Qualitatively the In/PCl<sub>3</sub>/H<sub>2</sub> and In/PCl<sub>3</sub>/Inert gas systems are similar to the corresponding Ga-As systems. Programs for these systems were included in the computer program.

#### THE COMPUTER PROGRAM

The computer program was designed for use with a Hewlett-Packard Model 9825T Calculator. The program contains four main systems:

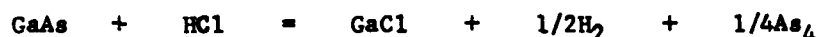
1. Ga/AsCl<sub>3</sub>/H<sub>2</sub>, inert gas
2. Ga/AsCl<sub>3</sub>/inert gas
3. In/PCl<sub>3</sub>/H<sub>2</sub>, inert gas
4. In/PCl<sub>3</sub>/inert gas

Each system includes subroutines for determining the degree of supersaturation in the deposition region and gives information regarding etching and relative growth rates. Each system also provides for the reactions involving silicon compounds

isoelectronic with InP and their formula weights differ by only 3 mass units. With the large numbers of FEF functions used, it was convenient to reduce them to a common polynomial and avoid interpolation during each set up calculations.

Errors in FEF and  $H_{298}^0$  are magnified in computing  $K_{eq}$ . The errors in FEF are small, but major discrepancies exist in some of the enthalpy values.

An important example in the Ga-As system is the choice of the enthalpy value for reaction (4). Although more recent values (Table II B.) are available, most authors continue to use the value of  $H_{298}^0 = 73.5$  kcal/mole calculated from the data in Stull and Sinke<sup>20</sup>. This is the origin of the common procedure of setting the  $As_4$  partial pressure nearly equal to one fourth of the input value of  $AsCl_3$  and the continued use of the reaction



to describe the transport and deposition reactions of gallium and arsenic.

Values for the  $As_2/As_4$  ratio at various temperatures and  $AsCl_3$  input are listed in Table III. These ratios show that at high temperatures  $As_2$  is equal to or more important than  $As_4$  whereas the latter is still the predominant species at lower temperatures. Ban<sup>10</sup> observed an  $As_2/As_4$  ratio of 1.6 at 850°C and a total  $AsH_3$  input of  $1.6 \times 10^{-2}$  atm. This is somewhat higher than the value of 0.73 calculated for these conditions. However from his  $As_2$  and  $As_4$  values  $H_{298}^0 = 46.7$  kcal/mole which is close to the maximum enthalpy value of 48.5 kcal/mole proposed by Joyce, Foxon and Wood<sup>63</sup>. These authors also find that only  $As_2$  is important above 600 K in the MBE of GaAs. In a systematic study of the rate of growth of GaAs Shaw<sup>64</sup> found that below 775-750°C the growth rate is kinetically controlled with an activation energy of 49 kcal/mole. Thus it is possible that at low temperatures the rate determining step in the formation of GaAs by CVE is the conversion of  $As_4$  to  $As_2$ .

A second discrepancy is in the choice of the enthalpy of formation of the



and intentional dopants. Variables include the temperatures of the source, the reactor tube along the furnace profile and the growth region, the vapor pressure and flow rates at each bubbler, the composition of the carrier gas, the atomic fractions of arsenic and phosphorus in gallium and indium, respectively. The program also permits the determinations of the concentrations of volatile silicon compounds at any point in the reactor and the dopant reactions. Because the experiments in Electronics Laboratory are performed in an open tube reactor, the total pressure in the program was arbitrarily set at one atmosphere and the concentrations of the volatile components are calculated in atmospheres.

The major assumption in this program is that equilibrium is established at the hot surfaces in each region of the reactor through heterogeneous catalysis. The method of calculation involved the determination of individual species by the method of iterative approximations rather than by minimizing the total Gibbs free energy<sup>18</sup>. The latter implies a closed system and may lead to results which are inconsistent with the open tube experiments.

In general the calculations obtained here agreed with those reported in the literature. Major differences reflect choice of thermodynamic values, the reaction model and the methods of calculation. These differences are discussed below.

Equilibrium constants were calculated from the relationship

$$21. \log K = ((FEF) - H^{\circ}_{298}/T)/2.303R$$

where  $R$  is the gas constant,  $H^{\circ}_{298}$  is the standard enthalpy of formation at 298 K and  $FEF$  is the Gibbs free energy function. The latter is defined by

$$22. FEF = - (F - H^{\circ}_{298})/T$$

where  $F$  is the Gibbs free energy. Values of  $FEF$  and  $H^{\circ}_{298}$  were taken from standard compilations, recent literature and, in some instances, calculated from either heat capacity or spectroscopic data (Table I). Because the required data for InP is not available, the heat capacity data for AlSb was used. AlSb is

silicon dioxide in the reactor tube. Because of the persistent use of the emphanism "quartz" for silica glass most authors <sup>12,65,66</sup> select the incorrect value for the enthalpy of formation of  $\text{SiO}_{2,g}$ . Table IV lists the concentrations of volatile silicon compounds formed in the reactions between HCl and silica glass in the hot reaction tube using different enthalpy values. Typical source conditions (850°C, 1 atm  $\text{H}_2$ , .00546 atm  $\text{AsCl}_3$ ) were employed in these calculations. Because the same conditions occur when the  $\text{AsCl}_3$  from the growth and etch bubblers enter the hot reactor no allowance for reactions with the source material were made. Column two and three list the calculated concentrations of silicon compounds based on enthalpy values of -215.6 kcal/mol (quartz) and -202.5 kcal/mol (silica glass), respectively. By using the former enthalpy value the amount of the silicon compounds formed and the amount of Si-doping is underestimated by a factor of ten.

The effects of varying the concentrations of  $\text{AsCl}_3$  (and HCl) and of hydrogen using a  $\text{H}_2$ -inert carrier gas on the formation of silicon compounds has been examined. In addition the effects of  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{NH}_3$  were calculated. Finally a study was made of the reactions of silicon compounds formed in the reactor with Ga, GaAs and  $\text{Ga}_{1-x}\text{As}_x$ . Typical caluclations showing the effect of  $\text{AsCl}_3$  in 1 atm  $\text{H}_2$  at 850°C are given in Table V. Increasing the  $\text{AsCl}_3$  input increases the formation of HCl by reaction (1). This results in an increase in the concentration of  $\text{SiCl}_4$  and  $\text{SiHCl}_3$ . The concentration of  $\text{SiH}_2\text{Cl}_2$  is nearly constant while the concentration of  $\text{SiH}_3\text{Cl}$  decreases. The latter represents the effect of the simultaneous increase in  $\text{H}_2\text{O}$  with an increase in  $\text{SiCl}_4$ . The major effect of increasing concentrations of HCl is the rapid decrease in the remaining silicon compounds:  $\text{SiH}_4$ , SiO and elemental silicon gas.

Changing the hydrogen content of the carrier gas also has a marked effect on the formation of silicon compounds. Typical data are given in Table VI. The concentrations of silicon compounds listed in column four are the same as those

given in column three of Table IV. The values in column two are for a ten percent excess of hydrogen over that required for the reaction with  $\text{AsCl}_3$ . As long as there is an excess of hydrogen, the concentration of  $\text{SiCl}_4$ , and therefore the total amount of silicon compounds and water vapor, is very nearly constant over a one hundred-fold change in the  $\text{H}_2$  concentration. However, decreasing the hydrogen concentration decreases the concentration of the remaining compounds. Again the effect is most noticeable with  $\text{SiH}_4$ ,  $\text{SiO}$  and  $\text{Si}$ . In the complete absence of hydrogen, i.e. the inert gas systems, the only volatile silicon compound present is  $\text{SiO}$  from reaction (9).

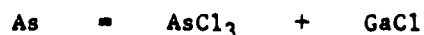
Oxygen reacts with hydrogen to form water. Thus either oxygen or water may be added along with the carrier gas to repress the formation of volatile silicon compounds. There are some practical considerations here, e.g. avoiding mixing hydrogen with oxygen and water with arsenic trichloride. Ammonia will react with the hot silica glass to form water and silicon nitride. Not only will the water

$$23. \quad 3\text{SiO}_2 + 4\text{NH}_3 = \text{Si}_3\text{N}_4 + 6\text{H}_2\text{O}$$

repress the formation of the volatile

silicon compounds, but the silicon nitride will coat the reactor and have the potential of rendering the reactor inert to further reactions with hydrogen and hydrogen chloride. Because the sublimation temperature of ammonium chloride is  $335^\circ\text{C}$ , the reaction between ammonia and hydrogen chloride in the hot reactor can be ignored.

An attempt was made to develop models for the reactions between  $\text{HCl}$  and the source materials. Model I corresponds to reaction (13) and assumes that only solid  $\text{GaAs}$  reacts with  $\text{HCl}$ . This is the condition Shaw<sup>16</sup> used in his calculations for a single phase system. Under these conditions the total arsenic in the gas phase is given by



where  $\text{AsCl}_3$  is the input from the bubbler and  $\text{GaCl}$  is the amount of gallium chloride formed in the reaction.

Model II corresponds to reaction (14) and assumes a uniform, thin crust of GaAs throughout the entire growth period of the epi layer. Under these steady state conditions, i.e.  $d(\text{GaAs}/dt) = 0$ , the mass balance for arsenic is given by

$$\text{As} = \text{AsCl}_3 + x\text{GaCl}$$

where  $x$  is the atom fraction of dissolved arsenic in the liquid phase,  $\text{Ga}_{1-x}\text{As}_x$ .

Model III corresponds to reaction (15) and assumes that gallium diffuses through the crust and reacts with HCl and arsenic forms GaAs. In this model the liquid phase is represented by  $\text{Ga}_{1-2x}(\text{GaAs})_x$ , the crust thickens and the mass balance for arsenic is given by

$$\text{As} = \text{AsCl}_3$$

The values for the Ga/As ratios for the three models are listed in Table VII. In making these calculations it was assumed that equilibria occurred between the gas and condensed phases. A second assumption is that the atom fraction of arsenic in  $\text{Ga}_{1-x}\text{As}_x$  is constant and that the liquid phase is in equilibrium with the crust material. Under these conditions the free energy of dissolved GaAs is equal to that of the crystalline material, the product of the activities of gallium and arsenic in the liquid phase is equal to one and the standard state of arsenic in the liquid phase is the saturated solution.

The value of "0.75" for the Ga/As ratio is due to the fact that in Model I one atom of arsenic would enter the vapor phase for each molecule of  $\text{GaCl}$  formed. Because of the small values of the atom fraction of arsenic in gallium at  $850^\circ\text{C}$  <sup>11,67</sup>, the Ga/As ratios in Models II and III are essentially those due to reaction (2). The difference in the Ga/As ratios for Models II and III is due to the slight increase in the amount of arsenic in the vapor phase in Model II (reaction 14).

Reaction (16) corresponds to a fourth model in which arsenic dissolves in

the liquid phase of a two-phase condensed system and crystallizes out as GaAs. The limiting condition for this model is a closed system in which the arsenic in the gas phase is in equilibrium with the condensed phases. These conditions qualify for use of the minimized Gibb's free energy technique used by Shaw <sup>16</sup> in making calculations for the two-phase system. They correspond to the conditions of no transport and no growth.

In addition, the silicon compounds formed by the reaction of HCl with the hot reactor also react with the source materials. The resulting concentrations of silicon compounds for different AsCl<sub>3</sub> input are listed in Table VIII in Table VIIIA. Model I was used as the basis for the calculations while the results using Model II are given in Table VIIIB. Results using Model III are not listed as they are essentially the same as for Model II.

The results using Model I, where the source reactant is GaAs, show that with this model the concentrations of the higher chlorosilanes increase rapidly with increasing AsCl<sub>3</sub> input while the concentrations of SiH<sub>4</sub>, SiO and Si decrease with increasing AsCl<sub>3</sub> input. With Model II, where no change occurs in the crust material, the concentrations of the chlorosilanes again increase with increasing AsCl<sub>3</sub> input. However with this model there is little or no change in the concentrations of SiH<sub>4</sub>, SiO and Si over a twenty fold change in the AsCl<sub>3</sub> input. This difference is due to the very small amount of HCl present in Model II. In fact the results for the Si calculations using Model II would suggest that increasing the AsCl<sub>3</sub> should have no effect upon unintentional Si-doping.

The computer program is designed to provide information regarding the relative rates of growth and whether etching will occur. Growth of the epi layer depends upon the fact that the equilibrium constant for reaction (3) increases with decreasing temperature. Thus a system saturated with respect to GaCl and As<sub>n</sub> at high temperatures will be supersaturated at lower temperatures and will either

form GaAs by nucleation or deposit GaAs on an exposed GaAs surface. For stoichiometric reasons the degree of supersaturation will be the smaller of either the GaCl or As concentrations in excess of that required for equilibrium at the lower temperature. The calculated relative growth rate will also depend on the model used. For example, using Model II etching should occur under typical experimental conditions (source 850°C, substrate 750°C, 1 atm H<sub>2</sub>, .00546 atm AsCl<sub>3</sub> from the growth bubbler) when the AsCl<sub>3</sub> from the etching bubbler reaches .002 atm. This is in good agreement with the experimental observations in the Electronics Laboratory and indicates that these calculations should be useful in the design of experiments with the two-boat, three bubbler system.

The computer program is also designed to study intentional doping. In particular the program can be used to study the reactions of the dopant in the gas phase and to calculate relative concentrations of reactants. The latter relationships provide information regarding the mechanism of the doping process.

For example, in one series of experiments Si-doped GaAs was grown on (100) substrates using H<sub>2</sub>S as the source of dopant. Two sets of experiments were run: the first was under normal growth conditions while in the second additional AsCl<sub>3</sub> was introduced from the etch bubbler. The results of these experiments are given in Table IXA and IXB. In both sets of experiments the ratio of  $n_d - n_a / H_2S$  was constant over a five fold change in H<sub>2</sub>S concentration. Similar results have been observed elsewhere<sup>68,69</sup>. However in the second set of experiments in the presence of additional AsCl<sub>3</sub>, the ratio of  $n_d - n_a / H_2S$  has decreased by a factor of nearly 7.4. This effect of AsCl<sub>3</sub> on S-doping was also observed by Heyen and co-workers<sup>69</sup> who found that the decrease was inversely proportional to the AsCl<sub>3</sub> input. The greater effect observed here is due to the fact that in this experiment the added AsCl<sub>3</sub> was introduced through the etch inlet whereas in the experiments by Heyen and co-workers the additional AsCl<sub>3</sub> was passed over the source

material. In the latter experiments the source material was saturated with arsenic at  $880^{\circ}$  and then cooled to  $850^{\circ}$  before beginning the growth experiments <sup>70</sup>. Under these conditions a considerable crust of GaAs will form corresponding to Model I. For this reason Model I was used in making the calculations for HCl given in Table IX.

If S-doping is thermodynamically controlled, reactions (18), (19), and (20) must be considered. The ratios of  $S/H_2S$ ,  $AsS/H_2S$  and  $Ga_2S/H_2S$  were calculated at each  $H_2S$  concentration. In all cases the ratios were constant over the range of  $H_2S$  used. The  $S/H_2S$  and  $AsS/H_2S$  ratios were independent of the added  $AsCl_3$ . However, the  $Ga_2S/H_2S$  ratio decreased by a factor of 6.9 which is in good agreement with the decrease in the value of  $n_d - n_a/H_2S$  in the two sets of experiments.

If  $Ga_2S$  is responsible for sulfur incorporation in the epi layer, then the sulfur will be on the arsenic site, the chemisorbed sulfur will be immediately bonded to three gallium atoms and the sulfur would be expected to have a high sticking coefficient. This is in agreement with the high values of S-dopant/ $H_2S$  ratios observed in Table IX and elsewhere <sup>68,69</sup>.

In the  $Ga/HCl/AsH_3/H_2$  system it can be easily shown that

$$Ga_2S/GaCl = K/C$$

where K is a constant incorporating the equilibrium constants for the above reactions, the  $H_2$  pressure and the partial pressure of  $H_2S$  and C is the HCl input. Thus in this system S-doping should be inversely proportional to the HCl input. It is possible that the data shown in Fig. 3 of reference (69) obeys this relationship.

#### DISCUSSION

When the source material is covered by a non-porous, uniform crust of GaAs, only reaction (13) occurs. When this reaction is complete, all of the GaAs will be removed, the liquid phase,  $Ga_{1-x}As_x$ , will be exposed and a discontinuity should occur in the vapor phase ratio of Ga/As. A discontinuity has not been observed either in the Ga/As ratio nor in the growth rate nor character of the epi layer. Instead

either a thin layer of GaAs or two phases are observed throughout the period of growth <sup>16</sup> .

If the physical fact of a thin crust is accepted as occurring throughout the period of growth, then reaction (13), the reaction with GaAs, and reaction (15), the formation of GaAs in the boat, must occur simultaneously. The overall reaction would be given by reaction (14) corresponding to the steady state condition. A requirement of the steady state condition is that the GaAs crust on top of the liquid phase is sufficiently porous that gallium can readily diffuse through the solid layer and account for 97-8 per cent of the total gallium found in the vapor phase.

An alternate steady state hypothesis involves three steps. First, GaAs reacts completely with HCl (or AsCl<sub>3</sub>) exposing the liquid phase. Second, the liquid phase reacts with HCl. Simultaneously arsenic in the vapor phase dissolves to form a supersaturated solution in gallium. In the third step nucleation occurs, a new crust of GaAs forms and the process is repeated. This would produce an oscillation in the Ga/As ratio in the arriving at the surface of the growing epi layer. This in turn may effect the stoichiometry of the epi layer and its electrical properties. Shaw <sup>16</sup> did observe an oscillation in the weight loss of a small (100 mg) drop of gallium but he could not observe a similar oscillation in the weight loss of a larger quantity of gallium in a boat nor did he correlate the oscillation in weight loss of the droplet with Ga/As ratios.

A third model involves the two condensed phases produced by a temperature gradient along the length of the source material. This model (reaction 16) requires a decrease of the arsenic in the vapor phase and a corresponding increase in the Ga/As ratio. This is in agreement with the observation that the cooled gallium will contain relatively massive crystals at one end and a thin crust at the other and that this observation can be used diagnostically to indicate a temperature profile.



The program and calculations described in the previous section are based on the assumption that thermodynamic equilibria is obtained. There are few data which can be used to test this assumption and, in every case, non-equilibrium conditions were reported. For example, Ban<sup>10</sup> examined reaction (2) using mass spectrophotometry and observed that the reaction was incomplete at useful flow rates. Shaw<sup>16</sup> found that the rate of growth of epi layers at temperatures above 775°C decreased with increasing AsCl<sub>3</sub> input. This effect could be partly obviated by increasing the area of the source material. Nonetheless above an AsCl<sub>3</sub> input of  $5 \times 10^{-3}$  atm growth rates still decreased indicating inefficient source reactions. DiLorenzo and Moore<sup>71</sup> determined the Ga/As ratio by measuring the weight loss of source materials at known AsCl<sub>3</sub> concentrations under typical growth conditions and found a ratio of 1.83-1.92 over a fivefold range of AsCl<sub>3</sub> input. Although this value is intermediate between that of about 0.75 for the reaction between HCl and GaAs and 2.83 for the reaction with a uniform porous crust of constant thickness, its constancy suggests that the reaction is kinetically controlled with the slow step first order with respect to AsCl<sub>3</sub>.

The AsCl<sub>3</sub> dependency of sulfur doping reported here and in reference 69 can be explained by the formation of Ga<sub>2</sub>S. Si-doping is also AsCl<sub>3</sub> dependent<sup>13,71</sup>. Recent experiments by Cox and DiLorenzo<sup>4</sup> who used a bypass AsCl<sub>3</sub> bubbler, show that unintentional Si-doping depends only upon the total AsCl<sub>3</sub>, i.e. chloride, introduced into the system. These results indicate that chlorosilanes do not react with the source materials. Instead they support the observations<sup>72</sup> regarding the dependency of silicon etching on HCl and the hypothesis that silicon is removed from the surface of the epi layer as SiCl<sub>2</sub>.

#### FUTURE WORK

A variety of CVE systems produce high quality epitaxial GaAs and each has its own inherent problems. Given the widespread study and commercial application of

the Ga/AsCl<sub>3</sub>/H<sub>2</sub> technique it would appear worthwhile to continue an examination of this system and to use it as a model for related systems. A large number of empirical observations have been made with this system on the conditions for GaAs growth rates. Yet few observations have been made regarding the source reactions and the volatile components within the reactor. For example, Shaw <sup>16</sup> implies that under appropriate conditions equilibrium will be established. On the other hand DiLorenzo and Moore <sup>71</sup> report that less than two-thirds of the HCl generated react with the source material while Feng et al <sup>14</sup> state that the amount of HCl leaving the boat region is equal to the amount of GaCl generated.

The value of the GaCl/As ratio is a function of the stoichiometry and extent of the reaction between the HCl (and AsCl<sub>3</sub>) and the source materials. It is necessary to standardize the boat conditions in order to be able to compare data obtained in different laboratories and to determine directly the extent of the source reactions and the amounts of HCl, GaCl and As reaching the substrate. It is only by quantifying the conditions within the reactor that we will be able to determine the rate laws for the determination of growth and thereby a better understanding of the growth process. It is anticipated that the latter will lead to the consistent preparation of high purity epitaxial GaAs.

At high temperatures GaCl <sup>73</sup> and As<sub>2</sub> <sup>74</sup> can be detected by vibrational raman spectroscopy which has a sensitivity at the parts per thousand level <sup>75</sup>. It would be worthwhile to initiate a series of experiments using this analytical method to determine the nature of the source reaction and the concentrations of the arsenic and gallium compounds involved in the CVD of GaAs using the Ga/AsCl<sub>3</sub>/H<sub>2</sub> technique.

# HIGH PURITY EPI SYSTEM

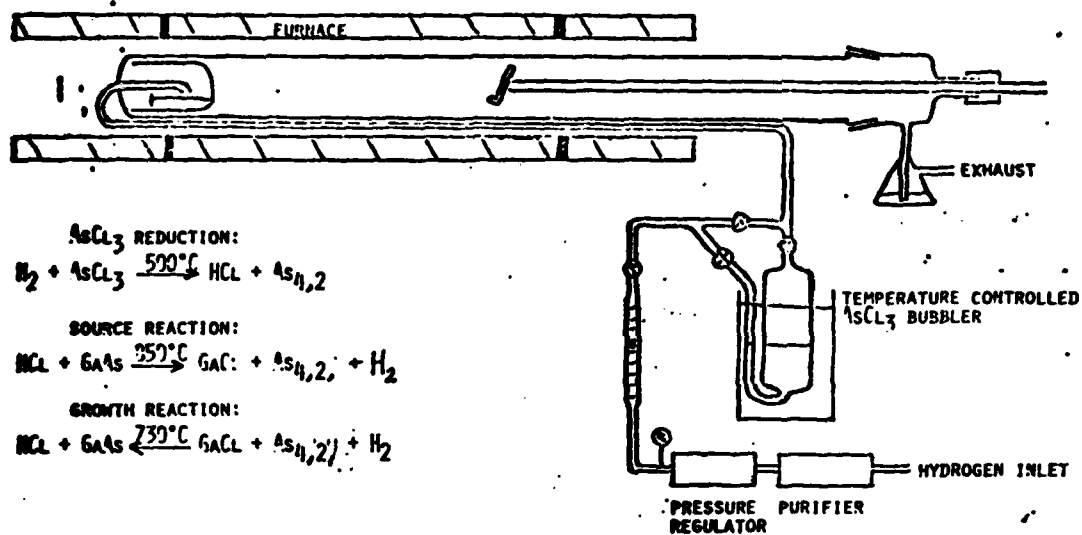


Figure 1

## PROPOSED FLOW SYSTEM

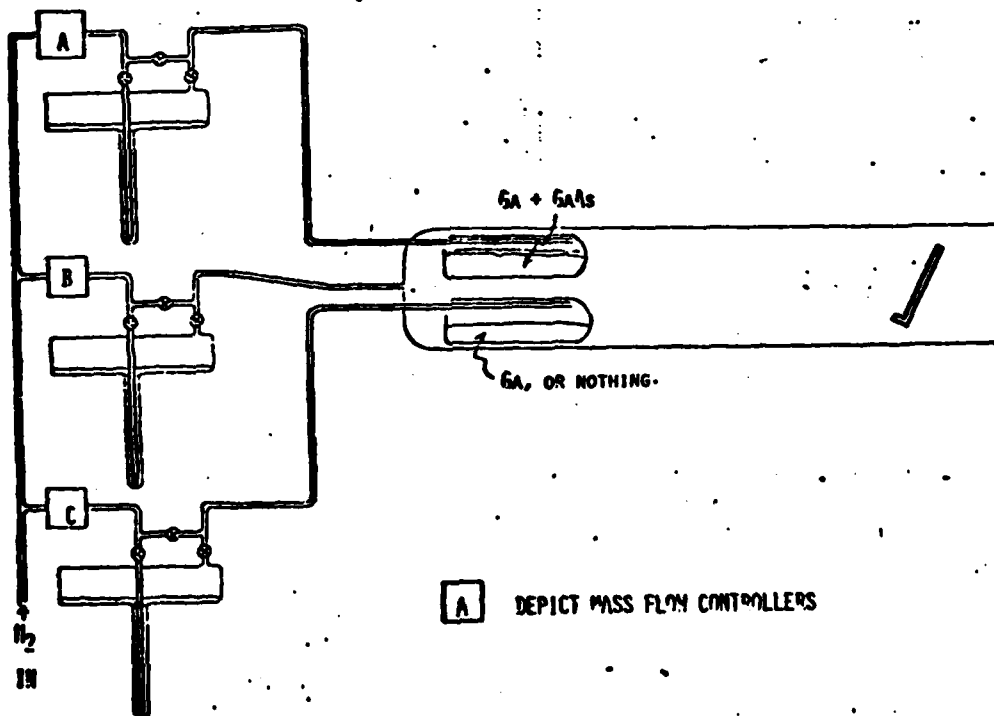


Figure 2

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Table I

Enthalpy Values and Sources of Thermodynamic Functions

<u>Substance</u>	<u>H°<sub>298</sub></u>		<u>Source</u>	<u>Ref.</u>
	<u>Value</u>	<u>Ref.</u>		
As, ref.			Tables	20
As <sub>2</sub>	45.54	21	Tables	20
As <sub>4</sub>	37.34	21		22
AsCl	28.00	23		23
AsCl <sub>3</sub>	-64.00	23	Spectroscopic data	24
AsS	25.00	25	Spectroscopic data	25
Cl <sub>2</sub>			Tables	26
Ga, l			Tables	20
Ga, v	65.00	19	Tables	20
GaAs	-21.70	27	Heat capacity	28
GaCl	-20.00	29		29
GaCl <sub>3</sub>	-102.00	29		29
Ga <sub>2</sub> O	-20.7	30		30
Ga <sub>2</sub> S	13.70	31	Spectroscopic data	31
H <sub>2</sub>			Tables	26
HCl	-22.06	26	Tables	26
H <sub>2</sub> O, g	-57.80	26	Tables	26
H <sub>2</sub> S	-4.88	26	Tables	26
In			Tables	20
InCl	-26.00	33	Spectroscopic data	32
InCl <sub>3</sub>	-102.25	33		34
InP	-15.4	35	Heat capacity <sup>a</sup>	36
NH <sub>3</sub>	-11.04	26	Tables	26
O <sub>2</sub>			Tables	26
P, red			Tables	26
P <sub>2</sub>	42.73	26	Tables	26
P <sub>4</sub>	30.77	26	Tables	26
PCl <sub>3</sub>	-61.03	26	Tables	26
S, rh			Tables	26

<u>Substance</u>	<u>H<sup>o</sup><sub>298</sub></u>		<u>FEF</u>	
	<u>Value</u>	<u>Ref.</u>	<u>Source</u>	<u>Ref.</u>
Si,s			Tables	26
Si,g	107.70	20	Tables	26
SiCl <sub>4</sub>	-157.10	26	Tables	26
SiHCl <sub>3</sub>	-119.30	37	Tables	26
SiH <sub>2</sub> Cl <sub>2</sub>	-75.29	37	Tables	26
SiH <sub>3</sub> Cl	-32.40	37	Tables	26
SiH <sub>4</sub>	8.20	38	Tables	26
SiO	-24.00	26	Tables	26
SiO <sub>2</sub> ,gl	-202.50	39	Tables	39
Si <sub>3</sub> N <sub>4</sub>	-127.00	26	Tables	26

<sup>a</sup>Data for InP unavailable. Used heat capacity data for AlSb.

Table II  
Choice of Enthalpy Values for the Reaction



A.  $\Delta H^\circ_{298} = 73.5 \text{ kc/mole, Ref } 20$

<u>Year</u>	<u>Reference</u>	<u>Reference Cited</u>
1964	40	20
1966	41	20
1968	42	40
1970	43	40
1970	44	20
1971	45	40
1971	10	44
1971	46	40
1972	47	20
1974	9	44
1975	48	43
1975	49	20
1975	50	43
1975	8	44
1976	51	50
1976	52	48
1976	53	44
1977	54	47
1978	55	44
1979	56	44
1980	57	44
1980	58	56
1980	14	44

Table II (cont.)

## B. Recent Experimental Values

<u>Year</u>	<u>Reference</u>	<u><math>\Delta H^\circ_{298}</math> kcal/mole</u>
1967	59	62.50
1973	60	54.26
1974	61	54.40
1975	21	53.74

C. Additional Choices of  $\Delta H^\circ_{298}$ 

<u>Year</u>	<u>Reference</u>	<u>Reference Cited</u>
1975	17	59
1976	62	60
1981	This Report	21

Table III

 $\text{As}_2/\text{As}_4$  Ratios for  $\text{H}^{\circ}_{298} = 53.74$ 

$\text{AsCl}_3$ Input, Atm.	$T^{\circ}\text{C}$				
	<u>700</u>	<u>750</u>	<u>800</u>	<u>850</u>	<u>900</u>
.001	.46	.973	2.07	4.52	10.15
.002	.31	.65	1.32	2.72	5.72
.003	.25	.52	1.03	2.06	4.18
.004	.22	.44	.87	1.70	3.38
.005	.19	.39	.76	1.48	2.87
.006	.175	.35	.69	1.32	2.53
.007	.16	.33	.63	1.20	2.28
.008	.15	.30	.58	1.10	2.08
.009	.14	.28	.55	1.03	1.92
.010	.13	.27	.51	.96	1.79

Table IV

The Enthalpy of  $\text{SiO}_2$  and Formation of Silicon Compounds

Temperature,  $850^\circ\text{C}$

$\text{AsCl}_3$  input, .00546 atm

$\text{H}_2$ , 1 atm

Concentration, Atm

$H^\circ_{298}$

Compound	-215.6 <sup>a</sup>	-202.5 <sup>b</sup>
$\text{SiCl}_4$	$3.0 \times 10^{-7}$	$2.2 \times 10^{-6}$
$\text{SiHCl}_3$	$7.5 \times 10^{-7}$	$5.3 \times 10^{-6}$
$\text{SiH}_2\text{Cl}_2$	$4.0 \times 10^{-8}$	$2.9 \times 10^{-7}$
$\text{SiH}_3\text{Cl}$	$1.2 \times 10^{-9}$	$8.9 \times 10^{-9}$
$\text{SiH}_4$	$5.2 \times 10^{-11}$	$3.7 \times 10^{-10}$
$\text{SiO}$	$4.9 \times 10^{-10}$	$2.5 \times 10^{-8}$
$\text{Si}$	$3.9 \times 10^{-18}$	$2.7 \times 10^{-17}$
$\text{H}_2\text{O}$	$2.2 \times 10^{-6}$	$1.6 \times 10^{-5}$
$\text{HCl}$	$1.6 \times 10^{-2}$	$1.6 \times 10^{-2}$

<sup>a</sup>Quartz

<sup>b</sup> $\text{SiO}_2$ , glass

Table V

Effect of  $\text{AsCl}_3$  Input on Si CompoundsTemperature,  $850^\circ$  $\text{H}_2$ , 1 atm $\Delta H^\circ_{298}$ ,  $\text{SiO}_2$  = -202.5 kcal/mole

<u>Compound</u>	Si Compound, Atm $\text{AsCl}_3$ , Atm		
	<u>0.001</u>	<u>0.004</u>	<u>0.016</u>
$\text{SiCl}_4$	$7.0 \times 10^{-8}$	$1.2 \times 10^{-6}$	$1.4 \times 10^{-5}$
$\text{SiHCl}_3$	$9.6 \times 10^{-7}$	$4.1 \times 10^{-6}$	$1.2 \times 10^{-5}$
$\text{SiH}_2\text{Cl}_2$	$2.8 \times 10^{-7}$	$3.0 \times 10^{-7}$	$2.0 \times 10^{-7}$
$\text{SiHCl}$	$4.8 \times 10^{-8}$	$1.3 \times 10^{-8}$	$2.2 \times 10^{-9}$
$\text{SiH}_4$	$1.1 \times 10^{-8}$	$7.0 \times 10^{-10}$	$3.1 \times 10^{-11}$
$\text{SiO}$	$1.3 \times 10^{-7}$	$3.4 \times 10^{-8}$	$7.3 \times 10^{-9}$
$\text{Si}$	$8.1 \times 10^{-16}$	$5.3 \times 10^{-17}$	$2.4 \times 10^{-18}$
$\text{H}_2\text{O}$	$2.9 \times 10^{-6}$	$5.5 \times 10^{-6}$	$1.1 \times 10^{-5}$
$\text{HCl}$	$2.99 \times 10^{-3}$	$1.2 \times 10^{-2}$	$4.8 \times 10^{-2}$

Table VI

The Effect of  $H_2$  on Si CompoundsTemperature,  $850^\circ C$  $AsCl_3$  Input, .00546 $\Delta H^\circ_{298}$ ,  $SiO_2$  = -202.5 kcal/mole

Compound	.00901 <sup>a</sup>	Concentration, Atm	
		$H_2$ , Atm	
		.1	1.0
$SiCl_4$	$5.1 \times 10^{-6}$	$4.4 \times 10^{-6}$	$2.2 \times 10^{-6}$
$SiHCl_3$	$1.1 \times 10^{-8}$	$1.0 \times 10^{-6}$	$5.3 \times 10^{-6}$
$SiH_2Cl_2$	$4.6 \times 10^{-13}$	$5.0 \times 10^{-9}$	$2.9 \times 10^{-7}$
$SiH_3Cl$	$1.2 \times 10^{-17}$	$1.44 \times 10^{-11}$	$8.9 \times 10^{-9}$
$SiH_4$	$4.0 \times 10^{-22}$	$5.5 \times 10^{-14}$	$3.7 \times 10^{-10}$
$SiO$	$3.0 \times 10^{-11}$	$3.3 \times 10^{-9}$	$2.5 \times 10^{-8}$
$Si$	$4.0 \times 10^{-23}$	$4.8 \times 10^{-19}$	$2.7 \times 10^{-17}$
$H_2O$	$1.0 \times 10^{-5}$	$1.1 \times 10^{-5}$	$1.6 \times 10^{-5}$
$HCl$	$1.64 \times 10^{-2}$	$1.64 \times 10^{-2}$	$1.64 \times 10^{-2}$

<sup>a</sup>10% excess over the amount required to react with  $AsCl_3$ .



Table VII

Ga/As Ratio as a Function of  $\text{AsCl}_3$ Temperature,  $850^\circ\text{C}$   
 $\text{H}_2$ , 1 atm

$\text{AsCl}_3$ , atm Model	Ga/As		
	<u>I</u>	<u>II</u>	<u>III</u>
.0005	0.74	2.83	2.99
.0025	0.73	2.83	2.99
.01	0.73	2.83	2.99
.02	0.73	2.83	2.99
"Completion"	0.75	2.91	3.00

Table VIII

## Effect of Source Material on Si Compounds

Temperature, 850°C

H<sub>2</sub>, 1 atm $\Delta H^\circ_{298}$ , SiO<sub>2</sub> = -202.5 kcal/moleA. Model IAsCl<sub>3</sub> Input

<u>Compound</u>	<u>0.001</u>	<u>0.005</u>	<u>0.02</u>
SiCl <sub>4</sub>	9.2x10 <sup>-12</sup>	1.0x10 <sup>-8</sup>	4.8x10 <sup>-7</sup>
SiHCl <sub>3</sub>	2.2x10 <sup>-9</sup>	3.0x10 <sup>-7</sup>	2.6x10 <sup>-6</sup>
SiH <sub>2</sub> Cl <sub>2</sub>	1.1x10 <sup>-8</sup>	2.0x10 <sup>-7</sup>	3.0x10 <sup>-7</sup>
SiH <sub>3</sub> Cl	3.4x10 <sup>-8</sup>	7.6x10 <sup>-8</sup>	2.0x10 <sup>-8</sup>
SiH <sub>4</sub>	1.3x10 <sup>-7</sup>	3.9x10 <sup>-8</sup>	1.8x10 <sup>-9</sup>
SiO	4.7x10 <sup>-7</sup>	2.5x10 <sup>-7</sup>	5.6x10 <sup>-8</sup>
Si	9.8x10 <sup>-15</sup>	2.9x10 <sup>-15</sup>	1.4x10 <sup>-16</sup>
H <sub>2</sub> O	8.3x10 <sup>-7</sup>	1.5x10 <sup>-6</sup>	6.8x10 <sup>-6</sup>
HCl	1.7x10 <sup>-4</sup>	1.3x10 <sup>-3</sup>	7.4x10 <sup>-3</sup>

B. Model II

SiCl <sub>4</sub>	3.6x10 <sup>-17</sup>	6.1x10 <sup>-12</sup>
SiHCl <sub>3</sub>	2.0x10 <sup>-13</sup>	1.6x10 <sup>-9</sup>
SiH <sub>2</sub> Cl <sub>2</sub>	2.3x10 <sup>-11</sup>	8.9x10 <sup>-9</sup>
SiH <sub>3</sub> Cl	1.6x10 <sup>-9</sup>	2.9x10 <sup>-8</sup>
SiH <sub>4</sub>	1.5x10 <sup>-7</sup>	1.3x10 <sup>-7</sup>
SiO	4.9x10 <sup>-7</sup>	4.7x10 <sup>-7</sup>
Si	1.1x10 <sup>-14</sup>	1.0x10 <sup>-14</sup>
H <sub>2</sub> O	7.9x10 <sup>-7</sup>	8.0x10 <sup>-7</sup>
HCl	7.4x10 <sup>-6</sup>	1.5x10 <sup>-4</sup>

Table IX

Carrier Conc.

$\text{H}_2\text{S Conc.} \times 10^{-8} \text{ atm.}$	$\left  \frac{n_d - n_s}{\times 10^{-16}} \right $	$\left  \frac{n_d - n_s}{-10^{-25}} \right  \text{H}_2\text{S}$
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A.  $\text{HCl}, 4.18 \times 10^{-3} \text{ atm}$ 

.81	2.0	2.5
1.13	3.0	2.65
1.58	3.5	2.2
2.24	6.0	2.7
3.19	10.0	3.13
3.8	8.0	2.1
	avg.	2.6

B.  $\text{HCl} = 1.12 \times 10^{-2} \text{ atm}$ 

.81	.2	.25
1.13	.5	.42
1.58	.5	.32
2.24	.9	.4
3.19	1.3	.41
3.8	1.7	.45
	avg.	.37